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13. ABSTRACT (Maximum 200 words) The first observation of J-aggregates of conjugated polymers in solution is reported. Concentrated solutions (1-8.8 mM) of conjugated polyquinolines 1a and 1b exhibited narrow, intense, and red shifted absorption bands, smaller Stokes shifts, and shortened fluorescence lifetimes, compared to isolated chains in dilute solution, which are characteristic of J-aggregation. In the solid state 1b formed highly luminescent J-aggregates whereas 1a formed excimers, reflecting the greater intermolecular distance in 1b . The excitonic delocalization size of the J-aggregates was estimated to be 15-24. These results provide new insights on the role of intermolecular interactions on the luminescence of conjugated polymers and have implications for the design of more efficient electroluminescent polymers, organic lasing materials, and cubic nonlinear optical materials.				
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J-Aggregates of Conjugated Polymers

By

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J-Aggregates of Conjugated Polymers

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Abstract

The first observation of J-aggregates of conjugated polymers in solution is reported. Concentrated solutions (1–8.8 mM) of conjugated polyquinolines **1a** and **1b** exhibited narrow, intense, and red shifted absorption bands, smaller Stokes shifts, and shortened fluorescence lifetimes, compared to isolated chains in dilute solution, which are characteristic of J-aggregation. In the solid state **1b** formed highly luminescent J-aggregates whereas **1a** formed excimers, reflecting the greater intermolecular distance in **1b**. The excitonic delocalization size of the J-aggregates was estimated to be 15–24. These results provide new insights on the role of intermolecular interactions on the luminescence of conjugated polymers and have implications for the design of more efficient electroluminescent polymers, organic lasing materials, and cubic nonlinear optical materials.

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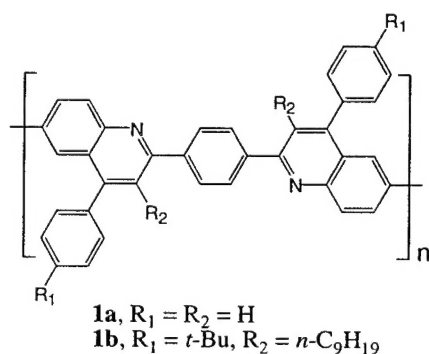
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The nature of the photophysics of conjugated polymers and how molecular and supramolecular structures influence it are questions of growing fundamental and practical interest.¹⁻⁶ Although conjugated polymers are promising for light-emitting diodes,⁷ solid state lasers,⁸ and xerographic photoreceptors,⁹ how to fundamentally improve their electronic and optical properties for these and other applications remains a challenging problem. Here, we report the first observation of J-aggregates of conjugated polymers in solution. We also show that J-aggregation and excimer formation in conjugated polymers can be regulated through side group substitution which controls the intermolecular distance in the solid state. The results provide new insights on the role of intermolecular interactions on the luminescence of conjugated polymers and have implications for the design of more efficient electroluminescent polymers, organic lasing materials, and cubic nonlinear optical materials.

The observation of new emission bands and significant luminescence quenching in thin films of conjugated polymers, compared to their dilute solutions, led to the suggestion^{1(a)} that “the fundamental approach to efficient photophysical processes in conjugated polymers is through control of the supramolecular structure and morphology of the materials.” Many experimental¹⁻⁴ and theoretical^{5,6} studies have since confirmed various effects of intermolecular interactions on the absorption and emission properties of conjugated polymers. Emissive excited state complexes (excimers, exciplexes)¹ and ground state complexes (“aggregates”)²⁻⁴ have been

reported in solid films of different polymers. One challenging question of continuing debate is how to distinguish excimers from aggregates of conjugated polymers.¹⁻⁶ The well-known characteristic absorption features of J- or H-aggregates of dye molecules¹⁰ have not yet been similarly observed in solution or solid state forms of conjugated polymers. Recently, laser-like emission spectral narrowing have been observed in various conjugated polymer thin films.⁸ One of the leading interpretations of this phenomenon is superfluorescence (SF) or superradiance (SR) that arises from cooperative emission from “aggregates”.^{8(b),11} However, the nature of the emissive aggregates is yet to be established. Studies aimed at a better understanding of the various electronic ground state and excited state supramolecular assemblies of conjugated polymers are thus warranted.



We investigated absorption and emission properties as a function of intermolecular separation in solutions and thin films of two conjugated polymers: poly(2,2'-(*p*-phenyl)-6,6'-bis(4-phenylquinoline)) (PPPQ, **1a**) and poly(2,2'-(*p*-phenyl)-6,6'-bis(3-(*n*-nonyl)-4-(*p*-*tert*-butyl)phenyl quinoline)) (BuN-PPQ, **1b**). We have previously reported the synthesis¹² and electroluminescent^{12(b),13} properties of **1a**, **1b**, and other related polyquinolines. Because of the side group substitutions in **1b** the minimum separation distance between adjacent chains is larger than in **1a**. By varying the concentration from $\sim 1\text{ }\mu\text{M}$ to 20 mM, based on repeat unit, we also

regulated the intermolecular separation between chains in formic acid solutions. Polymer thin films on silica substrates were spin coated from the most concentrated solutions and vacuum dried overnight at 60 °C to remove residual solvent. Photoluminescence emission (PL) and excitation (PLE) spectra were obtained at room temperature by using the front face configuration and a Spex Fluorolog-2 spectrofluorimeter. Details of PL decay dynamics measurement via laser excitation in time-correlated single photon counting experiments are as previously reported.¹⁴

The evolution of PLE spectra with solution concentration of **1a** is shown in Figure 1. In the most dilute solution (0.65 μM), a broad absorption band with λ_{max} at 407 nm and a full-width at half-maximum (FWHM) of 93 nm is observed in the PLE spectrum. We assign this to the spectrum of isolated chains of **1a**. The absorption spectrum (not shown) of this solution and other more concentrated ones were identical to this PLE spectrum. At higher concentration (9.8 μM), a Davydov split of the PLE spectrum into two narrow absorption bands with peaks at 330 and 436 nm is observed. The longer wavelength band is both narrower and more intense than the shorter wavelength component. Upon further increase of concentration to 8.8 mM the PLE spectrum showed only one intense absorption band with a peak at 466 nm and a FWHM of 19 nm. These excitation spectra features, particularly the narrow, red-shifted absorption bands of concentrated solutions, reveal *J-aggregation* of **1a**. Assuming that the exciton delocalization theory for dye aggregates is applicable to these *macromolecular aggregates*, the linewidth of the excitonic J band is expected to be narrower than that of the isolated molecule by $\sim N_c^{1/2}$ where N_c is the number of coherently coupled molecules in the aggregate.^{10(c)} We estimated $N_c = 24$ from the observed PLE linewidth of the 8.8 mM solution of **1a**.

The PL spectra of **1a** solutions were independent of concentration, having identical lineshape and emission peak at 498 nm (Figure 1, curves 4-6). The emission spectrum of **1a**

solutions was also independent of excitation wavelength, including direct excitation of the 436- and 466-nm peaks we assigned to J-aggregate bands. Taken together with the PLE spectra the Stokes shift thus decreased from 0.57 eV in the most dilute to 0.17 eV in the most concentrated. Vanishing Stokes shift, shortened fluorescence lifetime, and enhanced luminescence are commonly observed in the highly ordered and strongly coupled J-aggregates of dyes.¹⁰ The PL decay dynamics monitored at 498 nm (350-nm excitation) was essentially monoexponential for all three **1a** solutions. The fluorescence lifetimes were 0.80, 0.75, and 0.68 ns, respectively, shortening with increasing concentration. These steady-state PL spectra and fluorescence lifetime results are also consistent with J-aggregation.

Also shown in Figure 1 is the PL spectrum of **1a** thin film. The very broad emission band with peak at 578 nm is significantly red-shifted from the J-aggregate emission spectra in solution. The PLE spectrum corresponding to the 578-nm emission (not shown) was identical to that of the most dilute solution (Fig. 1, curve 1) except that an additional weak absorption in the 450-500 nm was seen. A huge Stokes shift of 0.91 eV was thus observed in **1a** thin film. The weak emission band in the ~450-500 nm region is in the same position as the J-aggregate emission in the concentrated solutions. These emission spectral characteristics suggest the presence of two emitting species in thin films, one is clearly J-aggregates which is also the minority component. The thin film PL decay dynamics was best described by two fluorescence lifetimes of 4.29 ns (57%) and 0.96 ns (31%). By comparison with the solution data, the species with 0.96-ns lifetime can be assigned to the J-aggregates. The long-lived, dominant species with a large Stokes shift can be assigned to excimers or excited state complexes. ^{1(a)}

The solution PLE and PL spectra of **1b** are shown in Figure 2. From similar arguments made for **1a**, we conclude that the sharp, narrowed, and red-shifted PLE spectrum of 1mM **1b**

evidence J-aggregates. In this case, the J-band at 397 nm has a FWHM of 20 nm compared to 78 nm linewidth of the 1 μ M solution PLE spectrum. From this we estimate the effective excitonic delocalization size (N_e) in **1b** aggregates to be 15. The PL spectra of **1b** were independent of concentration and they have a peak at 470 nm (Fig. 2, curves 4-6). Interestingly, the thin film PL spectrum of **1b** with a peak at 454 nm essentially overlaps the solution spectra but was more intense, suggesting J-aggregation. The thin film emission band is, however, broader due to a blue shoulder which may indicate different aggregate supramolecular structures. All the solution PL decay dynamics were very similar and can be approximately described by one lifetime as exemplified by 4.84 ns for the 1 mM J-aggregates. In contrast, the thin film PL decay was non-exponential with two main lifetimes: 60 ps (56%) and 410 ps (26%). The dramatically shortened lifetime and enhanced luminescence in **1b** thin film compared to solution confirmed its J-aggregate nature.

Comparison of results for **1a** and **1b** shows that both spontaneously formed J-aggregates in concentrated solutions. However, in the solid state **1b** formed highly luminescent J-aggregates whereas **1a** formed primarily excimers with a small amount of J-aggregates. These findings demonstrate the control of the photophysics of luminescent conjugated polymers through synthetic regulation of supramolecular structure. Furthermore, contrary to previous thought^{2,3} excimers can form in aggregated conjugated polymers.

In summary, we have observed J-aggregates of conjugated polymers in concentrated solutions and in solid films. Narrow and red-shifted absorption bands resolved by PLE spectroscopy, shortened excited state lifetimes, and enhanced luminescence, compare to isolated chains, were characteristic features of these *macromolecular* J-aggregates. Excimer formation by **1a** and J-aggregation of **1b** in the solid state demonstrated the synthetic control of intermolecular

distances in supramolecular assemblies of conjugated polymers. Block copolymer self-assembly of various supramolecular aggregate morphologies represents an approach that could be used to further manipulate these new forms of conjugated polymers.¹⁵ Based on dye molecule precedents,¹⁶ enhanced cubic nonlinear optical properties are anticipated in J-aggregates of conjugated polymers.

Acknowledgment. This research was supported by the Office of Naval Research and in part by the National Science Foundation (CTS-9311741, CHE-9120001).

Supporting Information Available: Figures showing thin film or solution UV-Vis, PLE, and PL spectra, PL decay dynamics of **1a** and **1b**, and their textural description (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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Figure Captions

Figure 1. PLE spectra (520-nm emission) of **1a** solutions (1) 0.65 μM , (2) 9.8 μM , (3) 8.8 mM; PL spectra (400-nm excitation) of **1a** solutions (4) 0.65 μM , (5) 9.8 μM , (6) 8.8 mM; and PL spectrum (400-nm excitation) of **1a** thin film (7).

Figure 2. PLE spectra (470-nm emission) of **1b** solutions (1) 1 μM , (2) 100 μM , (3) 1 mM; PL spectra (350-nm excitation) of **1b** solutions (4) 1 μM , (5) 100 μM , (6) 1 mM; and PL spectrum (350-nm excitation) of **1b** thin film (7).

Figure 1

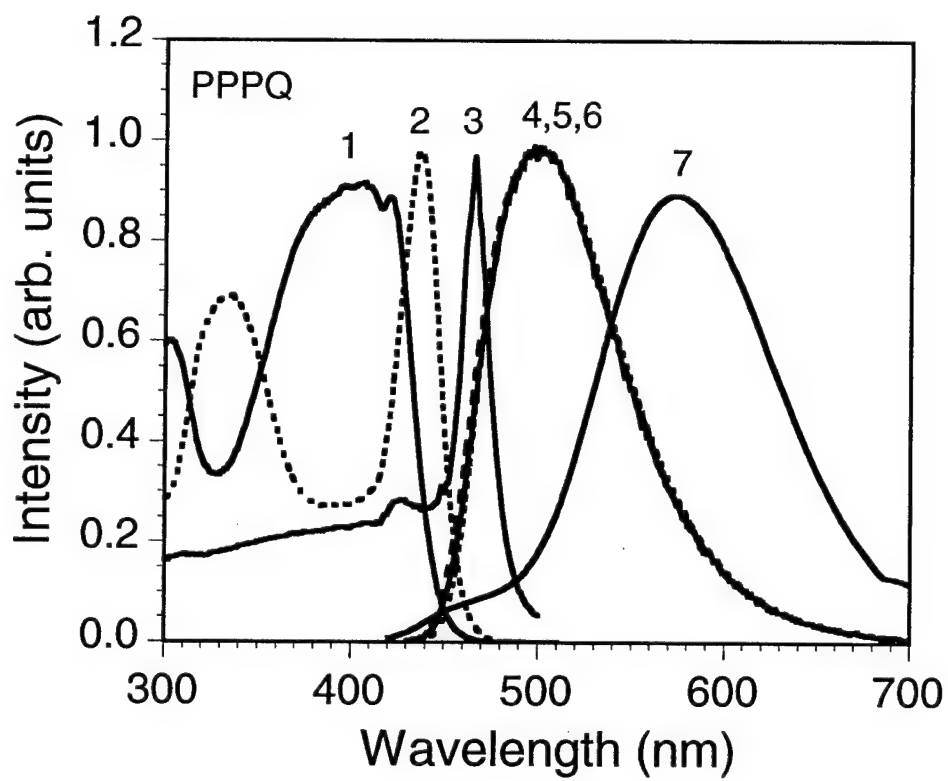
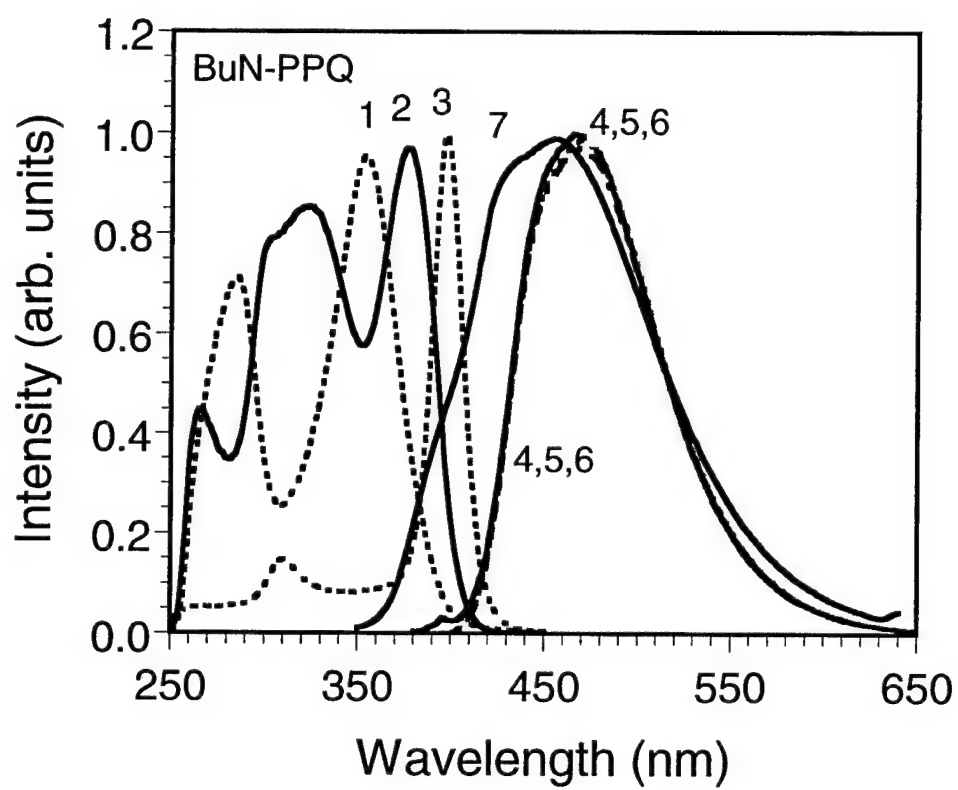


Figure 2



J-Aggregates of Conjugated Polymers

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Supporting Material

Figure S-1 shows optical absorption, PL, and PLE spectra of **1a** thin film on silica substrate. The excitation wavelength is 400 nm and the emission wavelength is 578 nm. The absorption spectrum shows two peaks at 400 and 300 nm. It also shows a relatively sharp absorption edge at 445 nm. The corresponding PLE spectrum tracks the absorption spectrum very well except that it showed a split (400 and 422 nm) in the main peak and a hump in the 450 to 500 nm region. These new features not observed in the absorption spectrum indicate existence of J-aggregates in **1a** (PPPQ) since the hump coincides with the J-aggregate band observed in solution PLE spectra. The PL spectrum of **1a** film with emission peak at 578 nm showed a large Stokes shift of 0.91 eV. This peak is also red-shifted about 70 nm compared to the aggregate emission peak (498 nm) in solutions. Therefore, the emission of **1a** thin film is due to excimers. In this respect, we point out two things. First, J-aggregates clearly exist in **1a** thin film as indicated by the 450-500 nm excitation and emission humps, but the emission is largely from excimers. Second, the J-aggregates are involved in excimer formation. This is evident from the independence of PL spectra with excitation wavelength (Figure S-2).

Absorption, PL, and PLE spectra of **1b** thin film are shown in Figure S-3. The absorption spectrum has two peaks at 275 and 347 nm. The PLE spectrum is identical to

the absorption except that the 347 nm peak is relatively more intense. The PL spectrum of **1b** has a peak at 454 nm. PLE spectra of two **1b** solutions (10 μ M and 20 mM) are also shown in Figure S-3. The 10 μ M **1b** solution has identical PLE spectrum to the 1 μ M solution with a peak at 353 nm. The 20 mM **1b** solution which is the most concentrated has a broad PLE spectrum with a peak at 360 nm. This rather broad excitation band suggests that considerable disorder has occurred; the supramolecular assemblies probably consists of more than one type of J-aggregate.

Time-resolved PL decay dynamics was measured by using the time-correlated single photon counting (SPC) technique. The excitation system consists of a cavity dumped dye laser (Coherent Model 703D) circulating rhodamine 6G, synchronously pumped by a mode-locked frequency doubled Nd:YAG laser (Quantronics Model 416). The dye laser pulses were typically 10 ps duration at a repetition rate of 38 MHz, and the samples were excited at 350 nm and monitored at the respective emission peaks of samples. The PL decay was detected at the emission peak wavelength. Figures S-4 to S-6 show PL decay dynamics of **1a** and **1b** solutions and thin films. For solutions, the decay dynamics can be best described by a single lifetime; for thin films, two lifetimes were needed to fit the data. The **1a** solutions showed lifetimes of 0.68, 0.75, and 0.80 ns, respectively, for concentrations of 8.8 mM, 9.8 μ M, and 0.65 μ M. The **1b** solutions showed lifetimes of 4.10, 4.84, 4.68, 4.72, and 4.72 ns, respectively, for concentrations of 20 mM, 1 mM, 0.1 mM, 10 μ M, and 1 μ M. The **1a** thin film had lifetimes of 4.29 (57% amplitude) and 0.96 ns (31%). The **1b** thin film had lifetimes of 410 (26%) and 60 ps (56%). The dramatic difference in fluorescence decay dynamics of **1a** and **1b** thin films is exemplified in Figure S-6.

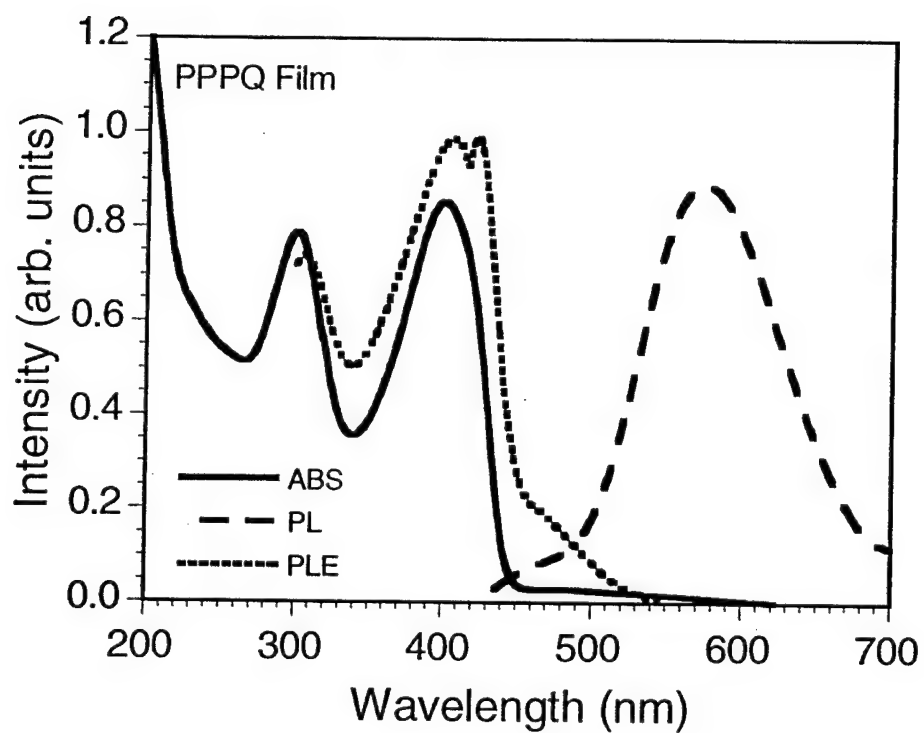


Figure S-1. Absorption, PLE, and PL spectra of **1a** (PPPQ) thin film on silica substrate.

The excitation wavelength for PL was 400 nm and the emission wavelength for PLE was 578 nm.

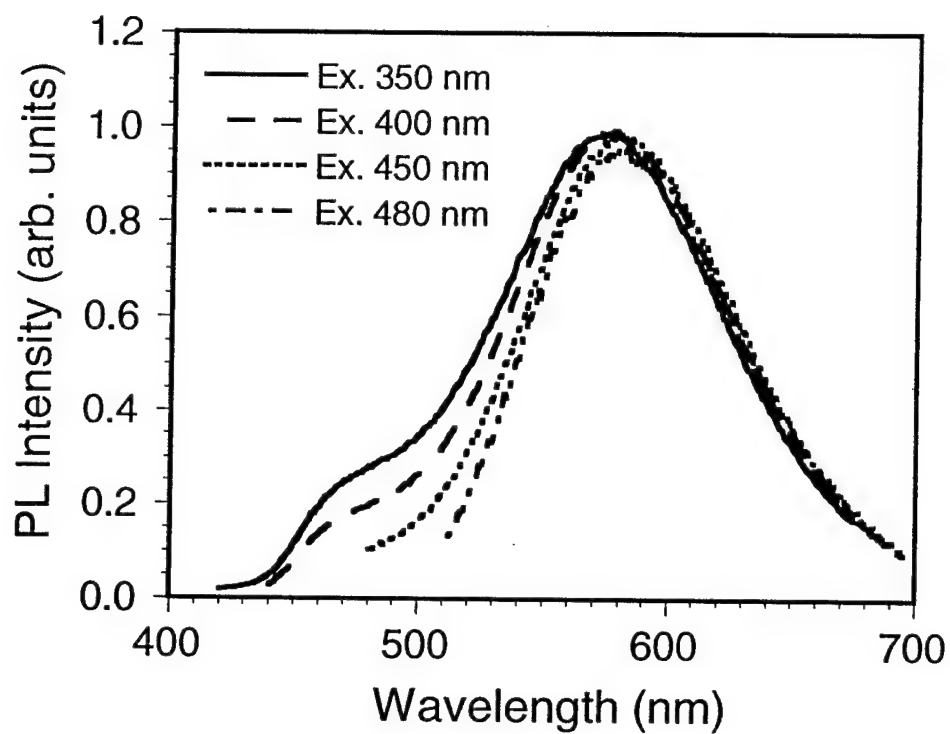


Figure S-2. PL spectra of **1a** (PPPQ) thin film with different excitation wavelengths in the range of 350–480 nm.

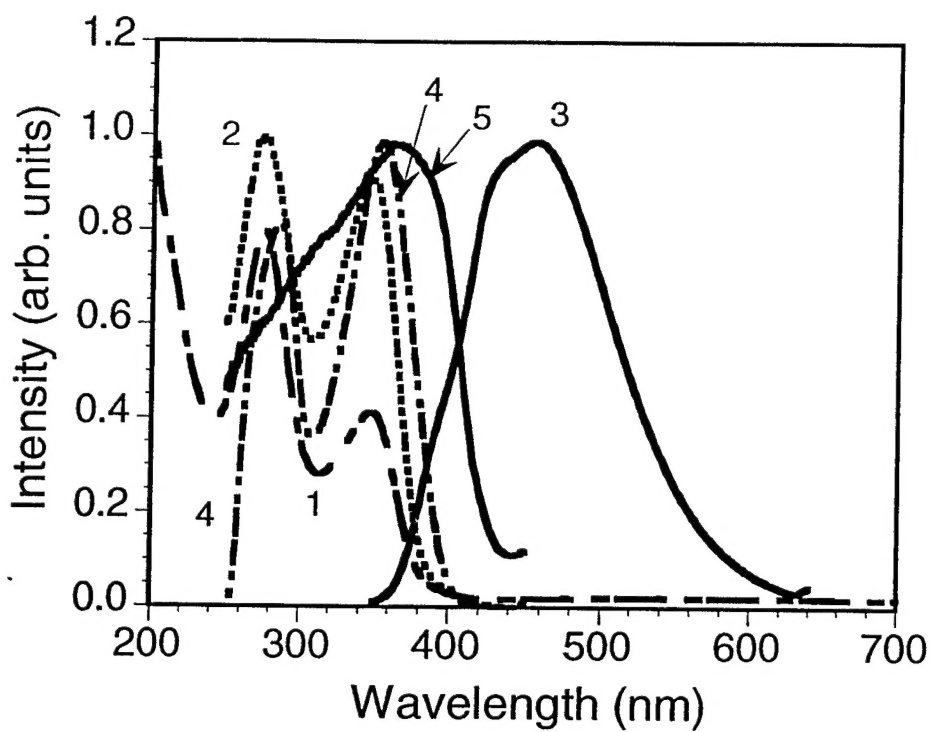


Figure S-3. Absorption (1), PLE (2), and PL (3) spectra of **1b** (BuN-PPQ) thin film on silica substrate and PLE spectra of **1b** in formic acid solutions of 10 mM (4) and 20 mM (5). The excitation wavelength was 350 nm, and the monitoring emission wavelength was 470 nm.

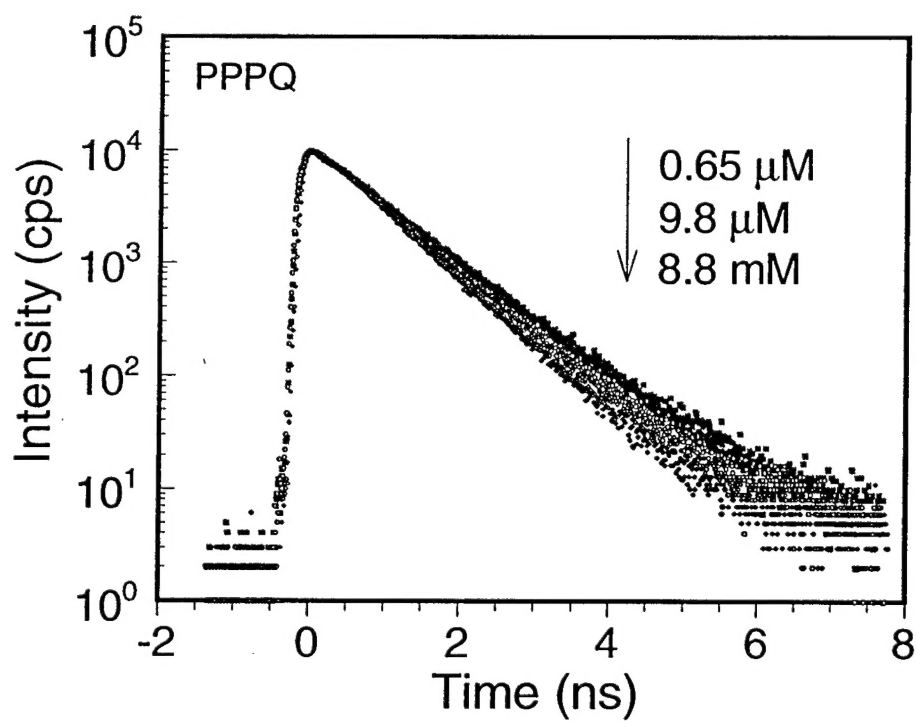


Figure S-4. Photoluminescence decay dynamics of **1a** (PPPQ) solutions in formic acid.

The excitation wavelength was 350 nm and the monitoring wavelength was 498 nm.

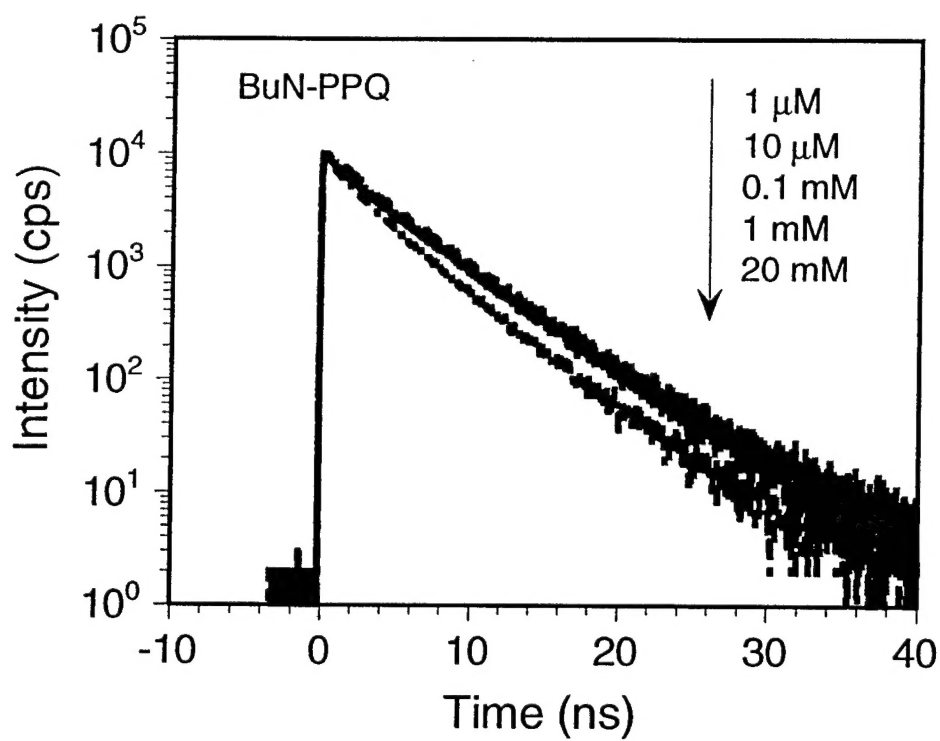


Figure S-5. Photoluminescence decay dynamics of **1b** (BuN-PPQ) solutions in formic acid. The excitation wavelength was 350 nm and the monitoring wavelength was 470 nm.

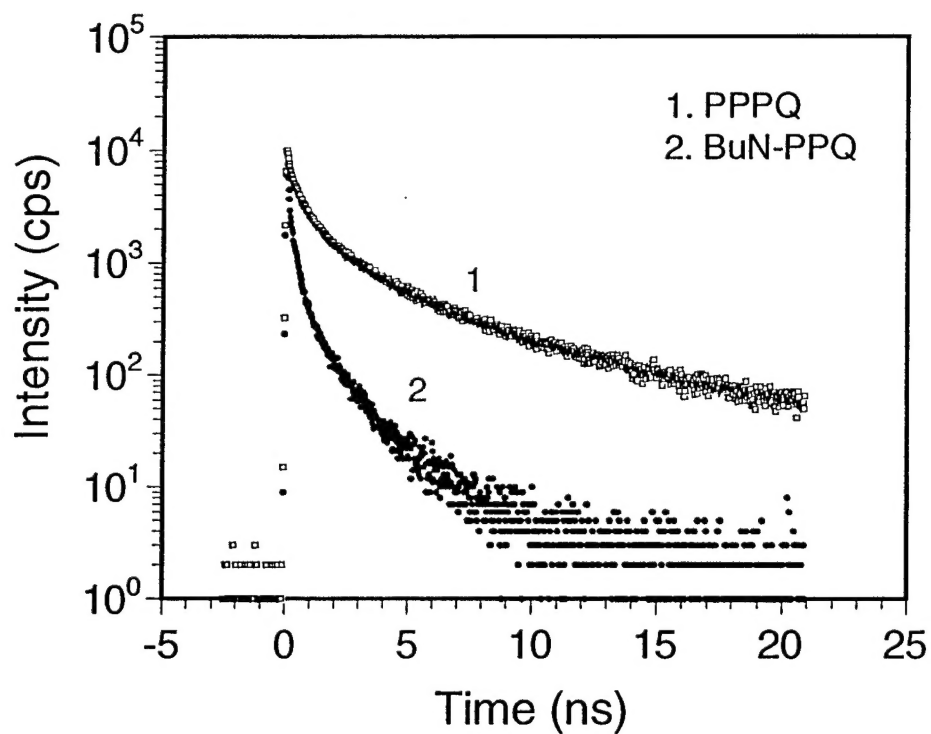


Figure S-6. Photoluminescence decay dynamics of **1a** (PPPQ) and **1b** (BuN-PPQ) thin films on silica substrates. The excitation wavelength was 350 nm. The monitoring wavelength was 578 nm for **1a** and 454 nm for **1b**.